

REMARKS

Applicants have amended their claims in order to a correct a typographical error in claim 10, and in order to add new claims 23-27 to the application. Claim 23 defines a method for manufacturing graphite powder, which includes processing steps of either claim 1 or claim 5. Thus, claim 23 is generic to claims 1 and 5. Claims 24 defines a method of manufacturing a lithium secondary battery which includes the fabricating, laminating and enclosing steps recited in each of claims 20 and 21, and specifies that the graphite powder (of the graphite electrodes) is manufactured by the method of claim 23. Claim 26 recites a method of manufacturing a lithium secondary battery, including the laminating and enclosing steps in each of claims 20 and 21, and recites that the graphite electrodes are manufactured by the granulating step recited in each of claims 20 and 21, the treating step of claim 20 or the immersing step of claim 21, and, after the treating or immersing step, the fabricating step recited in each of claims 20 and 21. Claims 25 and 27 respectively recite the lithium secondary battery manufactured by the process of claim 24 and claim 26.

The requirement for a Substitute Specification "excluding claims 1-22" is noted. Applicants are providing herewith such Substitute Specification, under 37 CFR 1.125(a).

The restriction requirement as set forth in the Office Action mailed August 31, 2000, is noted. Consistent with the requirement therein, Applicants respectfully elect the Group I claims, claims 1-4, which the Examiner has characterized as

being "drawn to a first method for making graphite powder". In addition, this restriction requirement is respectfully traversed, particularly insofar as applicable to the claims as presently amended.

In this regard, attention is respectfully directed to claim 23, reciting a method for manufacturing graphite powder, and including the processing steps of the Group I claims or the processing steps of the Group II claims. It is respectfully submitted that, in accordance with Group I and Group II, a graphite having a small fraction of rhombohedral structure can be obtained by the heat treatment of the Group I claims, or the immersing treatment of the Group II claims. As can be appreciated, the Group I claims and Group II claims provide a product having, in essence, a same structure. It is respectfully submitted that the processing of the Group I claims and of the Group II claims can properly be set forth in a same claim.

Moreover, note that claim 23 clearly links the Group I and Group II claims, and must be considered on the merits with the elected Group I claims. Upon allowance of, for example, claim 23, it is respectfully submitted that both the Group I and Group II claims should be allowed to issue in the same application.

Furthermore, it is respectfully submitted that especially in view of claims 23-27, the claims directed to a method for making the graphite powder, and claims directed to a method of making the lithium secondary battery and directed to the lithium secondary battery made, are sufficiently linked such

that all of the claims of Groups I-VII should be considered in the same application.

At the very least, Applicants note claims 20-22, directed to methods for making a lithium secondary battery, particularly as compared with claims 24 and 26. Note especially claim 24, reciting that the graphite powder of the graphite electrodes of the lithium secondary battery is manufactured by the method of claim 23. It is respectfully submitted that in accordance with the subject matter of Groups VI and VII, the secondary battery is manufactured using the graphite having a small fraction of rhombohedral structure, which is obtained by (1) a heat treatment, or (2) an immersing treatment. As stated previously, such graphite having the small fraction of rhombohedral structure, can be obtained by (1) the heat treatment or (2) the immersing treatment. Thus, particularly in view of newly added claims 23, 24 and 26, it is respectfully submitted that the methods of making the graphite powder and the methods for making the lithium secondary battery are sufficiently linked so that all of these claims (Groups I, II, VI and VII) should be considered on the merits in the present application.

In addition, it is again emphasized that the heat treatment and immersing steps recited in the present method claims provide a graphite having a small fraction of rhombohedral structure, which is utilized in the method of making a battery and used in the battery. It is respectfully submitted that particularly in view thereof, there is sufficient connection between the subject matter of the

various groups of claims as listed by the Examiner in Item 2 bridging pages 2 and 3 of the Office Action mailed August 31, 2000, such that all of the groups of claims should be considered in a single application. See Manual of Patent Examining Procedure 803.

In view of all of the foregoing, entry of the present amendments, reconsideration and withdrawal of the restriction requirement set forth in the Office Action mailed August 31, 2000, and consideration of all claims presently in the application, on the merits in the present application, are respectfully requested. At the least, it is respectfully requested that the Examiner reconsider the restriction requirement and consider all of the claims of Groups I, II, VI and VII, on the merits in the present application.

In any event, in order to provide a complete response to the Office Action mailed August 31, 2000, Applicants respectfully elect the Group I claims for prosecution on the merits in the present application, this election being made with traverse. Moreover, in addition to claims 1-4, it is respectfully submitted that claim 23 clearly falls within the Group I claims, and must be considered on the merits with the Group I claims.

To the extent necessary, Applicants petition for an extension of time under 37 CFR § 1.136. Please charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to the Deposit

Account No. 01-2135 (Case No. 503.34465VC3) and please credit  
any excess fees to such Deposit Account.

Respectfully submitted,

ANTONELLI, TERRY, STOUT & KRAUS, LLP



William I. Solomon  
Registration No. 28,565

1300 North Seventeenth Street  
Suite 1800  
Arlington, VA 22209  
Tel.: 703-312-6600  
Fax.: 703-312-6666

WIS/slk  
Enclosure



## Specification

## Title of the Invention

METHOD OF

NON-AQUEOUS SECONDARY BATTERY AND A MANUFACTURING

## 5 [METHOD OF] GRAPHITE POWDER

THIS application is a Divisional application of application Serial No. 08/1430,301 filed April 10, 1996.

## Background of the Invention

## [1] Field of the Invention:

The present invention relates to a carbon material which intercalates into or deintercalates from lithium, and to a method for manufacturing the same. In particular, the present invention relates to a lithium secondary battery, which uses [the] carbon material as a negative electrode active material, having a high energy density and a long life. The lithium battery is suitable for [using] in portable apparatus, electric automobiles, power storage, etc.

## [2] Description of the Prior Art:

The Lithium secondary battery using lithium metal for the negative electrode has some problems [in] safety. For example, lithium easily deposits like dendrite on the lithium metal negative electrode during [repeating charge] and [discharge] of the battery, and if the dendritic lithium [will grow] to a positive electrode, an internal short circuit [is] caused between the positive electrode and the negative electrode.

Therefore, a carbon material [is disclosed] as the negative electrode active material [replaceable] of lithium metal. Charge and discharge reactions [are] lithium ions

RECEIVED  
OCT 13 2000  
HALL ROOM

intercalation into the carbon material and deintercalation from the carbon material, and lithium is hardly [deposit] like dendrite. As for the carbon material, graphite is disclosed in JP-B-62-23433 (1987).

5       The graphite disclosed in JP-B-62-23433 (1987) forms an intercalation compound with lithium, because of intercalation or deintercalation of lithium. [The]graphite is used as a material for the negative electrode of the lithium secondary battery. In order to use [the above]graphite as the 10 negative active material, it is necessary to pulverize the graphite to increase <sup>the</sup> surface area of the active material, which [is] a charge and discharge reaction field, so as to allow [proceed]the charging and discharging reactions <sup>to proceed</sup> smoothly.

Desirably, it is necessary to pulverize the graphite to 15 powder having a particle diameter equal to or less than 100  $\mu\text{m}$ . However, as [it] is apparent from [a] fact that [the] graphite is used as a lubricating material, the graphite easily transfers its layers. Therefore, its crystal structure is changed by the pulverizing process, and formation of the 20 lithium intercalated compound might be influenced by undesirable effects? Accordingly, the graphite after the pulverizing process has a great deal of crystalline structural defects. In a case when [the above]graphite is used as an active material for the negative electrode of the 25 lithium secondary battery, a disadvantage [is caused] that a large capacity can not be obtained. Furthermore, preferable performances of rapid [charge and discharge] <sup>RESULTS IN</sup> charging and discharging are not obtained

because the lithium intercalation-deintercalation reaction is disturbed by the above defects.

#### Summary of the Invention

##### 5 [ (1) Objects of the Invention: ]

The object of the present invention is to solve the above problems [involved in the prior arts], to [disclose] a carbon material having a large lithium intercalation-deintercalation capacity and a method for manufacturing the same, and to provide a non-aqueous secondary battery which has a large capacity and is superior in [the] rapid charging and discharging characteristics using the above [disclosed] materials.

##### [ (2) Methods of solving the Problems: ]

15 The crystalline structure of the graphite powder relating to the present invention has a feature that an existing fraction of the rhombohedral structure in the crystalline structure of the graphite is small (equal to or less than 20 %). Another feature is that an existing fraction of the hexagonal structure is great (at least 80 %). The above existing fractions of the rhombohedral structure and the hexagonal structure can be determined by analyzing the intensity ratio of the peaks in [the] X-ray diffraction<sup>7</sup> of the material.

25 The graphite powder relating to the present invention is manufactured by a method comprising the steps of graphitizing treatment (heating at least 2000 °C) of raw

material such as oil cokes and coal cokes, pulverizing the graphitized raw material to powder, sieving the powder for obtaining the maximum particle diameter equal to or less than 100  $\mu\text{m}$ , heating the powder <sup>at least 900 °C</sup> as a heat treatment, and further heating the powder <sup>at least 2700 °C</sup> for eliminating impurities such as Si. For instance, when the powder is heated <sup>at least 2700 °C</sup>, Si, which is a main component of <sup>the</sup> impurities, can be reduced to less than 10 ppm. The heat treatment of the powder for eliminating impurities can be omitted depending on the content of the impurities in the raw material. In the pulverizing process, various conventional pulverizers can be used. However, a jet mill is preferable, because pulverization with the jet mill generates the minimum destruction of the graphite crystalline structure in the raw material.

Furthermore, the graphite powder relating to the present invention can be obtained by immersing into an acidic solution containing at least one compound selected from a group <sup>consisting</sup> consisted of sulfuric acid, nitric acid, perchloric acid, phosphoric acid, and fluoric acid as an immersing treatment, after pulverizing the raw graphite to obtain graphite powder having a particle diameter equal to or less than 100  $\mu\text{m}$ , subsequently washing with water, neutralizing, and drying.

The non-aqueous secondary battery for achieving the object of the present invention can be manufactured by using the graphite powder relating to the present invention as the

negative electrode active material, and the positive electrode is desirably composed of a material comprising a compound expressed by a chemical formula of  $\text{Li}_x\text{MO}_2$  (where; X is in a range from zero to 1, and M is at least any one of chemical elements selected from a group of Co, Ni, Mn and Fe), or  $\text{LiMn}_2\text{O}_4$ , that is a lithium transient metal complex oxide.

The active materials for the battery are generally used in [a] form of powder in order to [proceed] the charging and discharging reaction by increasing the surface area of the active material, which [is] a reaction field of the charging and discharging reaction. Therefore, the smaller the particle size of the powder is, the more will performance of the battery be improved. Furthermore, when the electrode is manufactured by applying an agent mixed with the active material and a binding agent to a current collector, the particle diameter of the active material is desirably equal to or less than 100  $\mu\text{m}$  in view of applicability and maintaining preciseness of thickness of the electrode.

As for the negative electrode active material for the lithium secondary battery, natural graphite, artificial graphite, and others are disclosed. However, for the above described reason, it is necessary to pulverize these materials. Therefore, in the pulverizing process, various graphite [powder] having a diameter equal to or less than 100  $\mu\text{m}$  were prepared with various pulverizing methods using a ball mill, a jet mill, a colloidal mill and other apparatus, for various [time]. And, the lithium intercalation-deintercalation

capacity of the various graphite [powder] were determined for  
[determining] <sup>powders</sup> [searching] a superior material for the negative electrode  
material of the lithium secondary battery.

However, the graphite powder obtained by the above  
5 method had [the] lithium intercalation-deintercalation amounts  
per weight in a range of 200-250 mAh/g, and their capacities  
as the material for the negative electrode of the lithium  
secondary battery were not enough.

In order to investigate the reason for the small  
10 capacity, crystalline structures of the above various  
graphite <sup>samples</sup> were determined by an X-ray diffraction method.  
FIG. 1 indicates an example of the results. Four peaks can  
be observed in a range of the diffraction angle ( $2\theta$ ,  $\theta$ :  
Bragg angle) from 40 degrees to 50 degrees in the X-ray  
15 diffraction pattern. The peaks at approximately 42.3 degrees  
and 44.4 degrees are diffraction patterns of <sup>the</sup> (100) plane and <sup>the</sup>  
(101) plane of hexagonal structure of the graphite,  
respectively. The peaks at approximately 43.3 degrees and  
20 46.0 degrees are diffraction patterns of <sup>the</sup> (101) plane and <sup>the</sup>  
(102) plane of rhombohedral structure of the graphite,  
respectively. As explained above, it was apparent that there  
were two kinds of crystalline structure in the pulverized  
graphite.

Further, the existing fraction (X) of the rhombohedral  
25 structure in the graphite powder was calculated by the  
following equation (Equation 1) based on the data of the  
observed peak intensity ( $P_1$ ) of the (100) plane of the

hexagonal structure, the observed peak intensity ( $P_2$ ) of the (101) plane of the rhombohedral structure, and a theoretical relationship of the intensity ratio in the X-ray pattern of the graphite. As [the] result, it was revealed that [the] graphite having the rhombohedral structure was contained by approximately 30 % in all the graphite pulverized equal to or less than 100  $\mu\text{m}$  in particle diameter.

$$X = 3P_2 / (11P_1 + 3P_2) \quad \dots \text{(Equation 1)}$$

10

Similarly, the existing fraction (X) of the rhombohedral structure of the graphite powder was verified by the relationship of the observed peak intensity ( $P_1$ ) of the (100) plane of the hexagonal structure, the observed peak intensity ( $P_3$ ) of the (102) plane of the rhombohedral structure, and the theoretical relationship of the intensity ratio in the X-ray pattern of the graphite. In this case, the following equation 2 was used instead of the equation 1. As [the] result, it was confirmed that [the] graphite having the rhombohedral structure was contained by approximately 30 % in all the graphite pulverized equal to or less than 100  $\mu\text{m}$  in particle diameter.

$$X = P_3 / (3P_1 + P_3) \quad \dots \text{(Equation 2)}$$

25

The reason for [existing] the two kinds of crystalline structure is assumed that the graphite itself has a

lubricating property; and the original graphite having [the] hexagonal structure transforms to [the] graphite having [the] rhombohedral structure by the pulverizing process with strong shocks. [The graphite] powder [having] a few microns in particle diameter obtained by further continued pulverization had a significantly broadened X-ray diffraction peak ( $P_4$ ) at the (101) plane of the hexagonal structure, and it was revealed that the content of amorphous carbon in the graphite was increased because the half band width of the peak was increased. Accordingly, the reason for the small lithium intercalation-deintercalation capacity of the conventional graphite powder can be assumed<sup>1</sup> that the crystalline structure of the graphite has <sup>been</sup> transformed to the rhombohedral structure and generated the amorphous carbon, [and] <sup>to be due to the fact</sup> with the result that proceeding of the lithium intercalation-deintercalation reaction is disturbed by the rhombohedral structure and the amorphous carbon.

Analysis [on] the impurities of the graphite powder revealed that [the] impurities such as Si, Fe, and others were present in a <sup>large amount</sup> [contained] more than 1000 ppm. Naturally, in addition to the impurities contained in the raw material, impurities from processing apparatus, such as a ball mill, a jet mill, and the like, can be mixed into the graphite [at] the pulverizing process. Therefore, the influence of the above impurities can be assumed as another reason for the small capacity, in addition to the above formation of the rhombohedral structure and amorphous carbon.

In accordance with the present invention, [the] graphite powder having a particle diameter equal to or less than 100  $\mu\text{m}$ , wherein the content of the above described rhombohedral structure is less than 30 % and the content of the amorphous carbon is small, has been developed. Additionally, the content of Si in particular, which is the main component of the impurities in the graphite powder, has been decreased to an amount equal to or less than 10 ppm. Therefore, extremely high purity is one of the features of the graphite relating to the present invention. The particle diameter equal to or less than 100  $\mu\text{m}$  is determined with an intention to use the graphite for [the] battery, as described previously. Therefore, when the graphite of the present invention is used for other purposes [usages], the particle diameter of the graphite is not necessarily restricted to equal to or less than 100  $\mu\text{m}$ .

Hereinafter, details of the graphite powder relating to the present invention, and the method for manufacturing the same [is] explained.

Two methods (manufacturing method 1 and manufacturing method 2) for obtaining [the] graphite having a small fraction of the rhombohedral structure are disclosed.

(Manufacturing method 1)

As for raw material (raw graphite) for the graphite powder of the present invention, both natural graphite and artificial graphite can be used. In particular, flaky natural graphite is preferable. Among the [above] raw graphite, the one [of which] maximum diffraction peak in the

X-ray diffraction pattern by the CuK $\alpha$  line [is appeared] at a diffraction angle ( $2\theta$ ,  $\theta$ : Bragg angle) in a range [form] 26.2 degrees to 26.5 degrees, that is, <sup>where</sup> an interval between two graphite layers is equal to or less than 0.34 nm, is desirable. [Because], [the] graphite powder containing a small amount of the rhombohedral structure can be obtained from the high crystalline raw material.

As for the pulverizing apparatus for crushing the raw graphite to [the] particle diameter equal to or less than 100  $\mu\text{m}$ , a jet mill is desirable. The reason is that the amorphous carbon is generated less with the jet mill than <sup>in</sup> the case when another pulverizing apparatus is used.

The pulverized raw graphite (raw powder) contains [the] graphite having [the] rhombohedral structure by approximately 30 % as previously described. Then, in accordance with the present manufacturing method 1, the existing fraction of the rhombohedral structure is [decreased] by the following heat treatment.

The heat treatment is performed <sup>to</sup> at least 900 °C under an inert gas atmosphere. As for the inert gas, nitrogen gas, argon gas, and the like is used. The inert gas atmosphere can also be maintained by covering the raw powder with cokes to seal it from the atmosphere.

The heat treatment is the most important process in the present invention for transforming the rhombohedral structure to [the] hexagonal structure. It is necessary to perform the heat treatment after pulverization of the raw

graphite (more preferably, at the last stage of the graphite powder manufacturing process of the present invention).

If the heat treatment is performed before the pulverization of the graphite and subsequently the graphite is pulverized, [the] graphite powder containing [the] rhombohedral structure <sup>in a quantity</sup> as small as possible, which is the object of the present invention, can not be obtained. The graphite powder containing the rhombohedral structure graphite <sup>in a quantity</sup> as small as possible can be obtained only by <sup>employing</sup> the heat treatment after the pulverizing process (more preferably, at the last stage of the graphite powder manufacturing process of the present invention) as the present invention.

The raw graphite powder contains Al, Ca, Fe, and particularly [much] of Si, as impurities. The impurities can be eliminated by heating and sublimating the materials <sup>at least</sup> 2700 °C. Therefore, the heating temperature in the heat treatment is preferably at least 2700 °C in order to perform a purification treatment concurrently.

(Manufacturing method 2)

The raw graphite and the pulverizing process is [as] same as the above manufacturing method 1.

The graphite powder of the present invention can be obtained by treating the graphite powder obtained by the pulverizing process with an acidic solution containing at least one compound selected from a group <sup>consisting</sup> [consisted] of sulfuric acid, nitric acid, perchloric acid, phosphoric acid, and fluoric acid, and subsequently washing with water.

neutralizing, and drying. During the treatment, a compound is formed with anions in the above acidic solution and the graphite, and the rhombohedral structure graphite is eliminated by the formation of the compound. The anions from 5 the acidic solution in the compound are eliminated from the compound during the washing, the neutralizing, and the drying, and the graphite powder relating to the present invention can be obtained.

The crystalline structure of the graphite powder of the 10 present invention obtained by the above manufacturing methods 1 and 2 was analyzed by [an] X-ray diffraction. The ratio of [the]  $P_1$  and  $P_2$ , ( $P_2/P_1$ ), was less than 0.92, and the half band width of [the]  $P_4$  was less <sup>than 0.45</sup> degrees. The ratio of [the]  $P_1$  and  $P_3$ , ( $P_3/P_1$ ), was less than 0.75.

15 By substituting the above observed data for the equations 1 and 2, the fact that the existing fraction of the rhombohedral structure has been decreased <sup>to</sup> less than 20 % and the existing fraction of the hexagonal structure has been increased at least 80 % was confirmed. Simultaneously, 20 the content of Si was confirmed to be less than 10 ppm from the result of impurity analysis.

Then, an electrode was prepared using the graphite powder of the present invention as an active material, and the lithium intercalation-deintercalation capacity was studied. 25 As [the] result, the lithium intercalation-deintercalation capacity of the graphite powder of the present invention was 320-360 mAh/g per unit weight of the active material, and

the capacity was significantly improved in comparison with the capacity of the conventional graphite material (200-250 mAh/g). Furthermore, it was found that the preferable existing fraction of the rhombohedral structure was equal to 5 or less than 10 %, because the less the existing fraction of the rhombohedral structure in the graphite powder of the present invention is, the more will the capacity be increased. *insert in Prel. Amd.*

Accordingly, the rhombohedral structure is evidently a crystalline structure which hardly <sup>will</sup> intercalate or deintercalate lithium. Therefore, it is assumed that the high lithium intercalation-deintercalation capacity of the graphite powder of the present invention is achieved by especially decreasing the existing fraction of the rhombohedral structure and increasing the existing fraction 15 of the hexagonal structure.

The feature of the lithium secondary battery of the present invention is in using the graphite powder of the present invention as the negative active material. The lithium secondary battery relating to the present invention 20 has a large load capacity, and a high energy density can be realized.

As <sup>a</sup> result of an evaluation <sup>of</sup> [on] the characteristics of the lithium secondary battery of the present invention, it 25 was confirmed that the lithium secondary battery of the present invention had a superior performance in rapid charging and discharging characteristics, and <sup>a</sup> decreasing

ratio of the capacity was improved at least 30 % in comparison with the conventional lithium battery under a same rapid charging and discharging condition. The reason for the improvement can be assumed<sup>7</sup> to relate to the fact that the reversibility for the lithium intercalation-deintercalation reaction of the graphite of the present invention is improved in comparison with the conventional carbon material by decreasing the existing fraction of the rhombohedral structure and eliminating the influence of the impurities, such as Si.

As the positive active material for the lithium secondary battery of the present invention, materials such as  $\text{Li}_x\text{CoO}_2$ ,  $\text{Li}_x\text{NiO}_2$ ,  $\text{Li}_x\text{MnO}_4$ , (where, X is in a range 0-1) and the like are desirable because a high discharge voltage of at least 3.5 V can be obtained, and the reversibility of the [charge] and [discharging] of the positive electrode itself is superior.

As for the electrolytic solution, a mixed solvent composed of ethylene carbonate mixed with any one selected from a group [consisted] of dimethoxyethane, diethylcarbonate, dimethylcarbonate, methylethylcarbonate,  $\gamma$ -butyrolactone, methyl propionate, and ethyl propionate, and at least one of the electrolytes selected from a group [consisted] of salts containing lithium such as  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ , and the like are used. It is desirable to adjust the lithium concentration in a range 0.5- 2 mol/l, because, the electric conductivity of the electrolytic solution [is] favorably large.

Brief Description of Drawings

Figure 1 indicates an X-ray diffraction pattern of [the] conventional graphite;

5 Figure 2 indicates an X-ray diffraction pattern of [the] graphite powder relating to the embodiment 1 of the present invention (heat treatment temperature: 900 °C);

Figure 3 indicates an X-ray diffraction pattern of the graphite powder relating to the embodiment 1 of the present invention (heat treatment temperature: 2850 °C);

10 Figure 4 indicates an X-ray diffraction pattern of the graphite powder prepared in the comparative example 1;

Figure 5 indicates an X-ray diffraction pattern of the graphite powder relating to the embodiment 2 of the present invention;

15 Figure 6 [indicates] a schematic cross section of the battery used in the embodiment 3 and the comparative example 2;

Figure 7 is a graph indicating a relationship between the electrode potential and the lithium intercalation-deintercalation capacity;

20 Figure 8 is a partial cross section of the lithium secondary battery prepared in the embodiment 5 of the present invention;

Figure 9 is a graph indicating a relationship between the discharge capacity and the number of [repeating] the charge and the discharge cycles;

Figure 10 is a graph indicating a relationship between

the discharge capacity and the charging and discharging current,

#### Detailed Description of the Embodiments

5

Referring to drawings, embodiments of the present invention are explained hereinafter.

##### Embodiment 1

10 Flaky natural graphite which was produced from Madagascar was used as the raw material, and the raw material was pulverized to powder, of which particle diameter was equal to or less than 46  $\mu\text{m}$ , by a jet mill. The powder was sieved to obtain raw material powder. The average 15 diameter of the raw material powder was 8.0  $\mu\text{m}$ .

Subsequently, the raw material powder was processed with a heat treatment by heating at 900 °C or 2850 °C for ten days under a nitrogen atmosphere, and the graphite powder of the present invention was obtained.

20 The crystalline structures of the graphite powder of the present invention and the raw material powder were analyzed by an X-ray diffraction method using an apparatus RU-200 made by Rigaku Denki, and the impurity content was analyzed by [an] inductively coupled plasma spectrometry (ICP) using an 25 apparatus P-5200 made by Hitachi.

The X-ray diffraction patterns of the graphite powder of the present invention, which have been observed under a

condition of X-ray tube voltage [40 kV], X-ray tube current [150 mA], and X-ray source [CuK $\alpha$  line], are shown in FIGs. 2 and 3. FIG. 2 is the pattern obtained by the heat treatment at 900 °C, and FIG. 3 is the pattern obtained by the heat treatment at 2850 °C. The X-ray diffraction patterns of the graphite powder of the present invention in both FIG 2 and FIG. 3 indicate that the peaks at diffraction angles of 43.3 degrees and 46.0 degrees, both of which belong with the rhombohedral structure, are decreased by either of the above 10 heat treatments.

The amount of Si contained in the graphite powder of the present invention as an impurity was 1140 ppm when the heating temperature was 900 °C, and 27 ppm when the heating temperature was 2850 °C. Therefore, it is revealed that a 15 highly purified graphite powder, of which Si is eliminated, can be obtained by heat treatment at a high temperature at least 2700 °C, by which Si can be eliminated.

#### Comparative example 1

In order to [compare] with the embodiment of the present invention, [the] non-pulverized raw graphite was heated at 2850 °C, and subsequently pulverized to obtain [the] graphite powder. The X-ray pattern of the graphite powder obtained by the above process is shown in FIG. 4. It is apparent from FIG. 4 that the peaks at diffraction angles of 43.3 degrees and 46.0 degrees, both of which belong [with] the rhombohedral structure, are not decreased. That means [that] the rhombohedral

structure can not be eliminated by the above process.

### Embodiment 2

In accordance with the embodiment 2, [the] raw graphite  
5 was pulverized by a jet mill to less than 100  $\mu\text{m}$  in particle  
diameter. Then, the graphite powder was immersed into a  
mixed acid<sup>of sulfuric acid and nitric acid</sup> for a whole day.  
Subsequently, washing with distilled water and  
neutralization with a dilute aqueous solution of sodium  
10 hydroxide were performed. The graphite powder obtained by  
the above process was dried at 120 °C to obtain the graphite  
powder of the present invention. The X-ray pattern of the  
graphite powder obtained by the above process is shown in  
FIG. 5. The peaks at diffraction angles of 43.3 degrees and  
15 46.0 degrees, both of which belong[with] the rhombohedral  
structure, are decreased. Accordingly, it was found that the  
rhombohedral structure was eliminated by the above process.

### Embodiment 3

20 In accordance with the embodiment 3, a carbon electrode  
was prepared using the graphite powder of the present  
invention as an electrode active material, and the lithium  
intercalation-deintercalation capacity, in other words, [a]  
load capacity of the negative electrode in the lithium  
25 secondary battery, was studied with the electrode.

Mixed agents slurry were prepared by mixing 90 % by  
weight in total solid of the graphite powder of the present

invention prepared in the embodiment 1, 10 % by weight of polyvinylidene fluoride (PVDF) as a binder, and N-methyl-2-pyrolidone, of which <sup>the</sup> heating temperatures were 900 °C and 2850 °C, respectively. The mixed agents slurry was applied on a plane of a sheet of copper foil of 10 µm [thick,] and dried in vacuum at 120 °C for one hour. After the vacuum drying, an electrode was fabricated by roller pressing, of which <sup>the</sup> thickness was in a range 85-90 µm. The average amount of the applied mixed agents per unit area was 10 mg/cm<sup>2</sup>. The electrode was prepared by cutting the copper foil [applied] with the <sup>applied</sup> mixed agents into a sheet of 10 mm X 10 mm.

FIG. 6 is a schematic cross section of a battery used for studying the lithium intercalation-deintercalation capacity of the present electrode. The battery has a structure, wherein a working electrode current collector 30, the electrode of the present invention 31, which is a working electrode, a separator 32, a lithium metal <sup>element</sup> 33, which is a counter electrode, <sup>and</sup> a counter electrode current collector 34 are piled and inserted into a battery vessel 35, and a battery lid 36 is screwed <sup>for</sup> fixing. A reference electrode made of lithium metal 37 is attached to the battery. As for the electrolytic solution, a mixed solvent of ethylene carbonate and diethylcarbonate (by) 1:1 in volume and lithium hexafluorophosphate were used with <sup>a</sup> lithium concentration of 1 mol/l.

The intercalation-deintercalation of lithium was repeated by applying a constant current between the working

electrode and the counter electrode, and the capacity was determined. The terminated potentials of the intercalation and the deintercalation of the working electrode were set as 0 V and 0.5 V, respectively.

5

Comparative example 2

In order to [compare] provide a comparison with the embodiment of the present invention, a carbon electrode was prepared with the graphite powder obtained in the comparative example 1 by the same method as the embodiment 3, and the load capacity (the amount of lithium intercalation-deintercalation) was determined. The same study was performed on the electrode prepared with the conventional graphite powder (the same powder as the raw powder in the embodiment 1).

15 A result of comparison on the lithium intercalation-deintercalation behavior of the electrode in the embodiment 3 (the present invention) with the electrode in the comparative example 2 (prior art) and the electrode prepared with the conventional graphite powder [is] explained  
will be  
with the conventional graphite powder [is] explained  
hereinafter. FIG. 7 is a graph indicating a relationship  
20 between the lithium intercalation-deintercalation capacity and [an] electrode potential at the fifth cycle, wherein the capacity becomes stable, after repeating the intercalation-deintercalation of lithium. In FIG. 7, the curve 40 indicates the potential variation of the electrode prepared  
25 with the graphite powder, of which heating temperature [at] during the heat treatment was 900 °C, in the embodiment 3. The curve

41 indicates the potential variation of the electrode prepared with the graphite powder, of which <sup>the</sup> heating temperature at ~~at~~ during the heat treatment is 2850 °C, in the embodiment 3. The curve 42 indicates the potential variation of the electrode prepared with the conventional graphite powder, and the curve 43 indicates the potential variation of the electrode prepared with the graphite powder which has been prepared in the comparative example 1 by the reversely ordered processes. The intercalation capacity and the deintercalation capacity for lithium in both the cases of using the conventional graphite in the comparative example 2 (the curve 42) and the graphite in the comparative example 1 (the curve 43) were less than 250 mAh/g per unit weight of the active materials. On the contrary, in the case of the embodiment 3 (the curves 40, 41), wherein the graphite powder prepared in the embodiment 1 was used as the active material, both the intercalation capacity and the deintercalation capacity for lithium were more than 300 mAh/g per unit weight of the active materials. That means, <sup>that</sup> a large load capacity was obtained by using the graphite powder having a small existing fraction of the rhombohedral structure relating to the present invention. Furthermore, the case (the curve 41) using the graphite powder highly purified by heating up to 2850 °C indicates the largest values in both the intercalation capacity and the deintercalation capacity for lithium in

FIG. 7.

## Embodiment 4

The embodiment 4 was performed in order to confirm the influence of treating time in the heat treatment of the present invention. In the embodiment 4, the graphite powder 5 of the present invention was obtained in [accordance with the] substantially <sup>the</sup> same manner as the embodiment 1 (under a nitrogen atmosphere, the raw powder was heated at 2850 °C). However, the treating time of the heat treatment was varied in a range from 0 hours to 30 days.

10 The existing fraction of the rhombohedral structure was determined from the peak intensity in X-ray diffraction patterns. Furthermore, as [same as] the embodiment 3, the electrodes were prepared with the obtained graphite powders, and the intercalation-deintercalation reactions of lithium 15 were repeatedly performed. The result on the lithium intercalation-deintercalation capacity at the fifth cycle is shown in Table 1.

Table 1

Heating time	The existing fraction of the rhombohedral structure (%)	Lithium intercalation capacity (mAh/g)	Lithium deintercalation capacity (mAh/g)
5	0 hours	27.3	235
	4 hours	18.2	320
	10 hours	14.6	325
	1 day	13.8	334
	3 days	11.3	338
	5 days	9.7	351
	10 days	7.1	360
	30 days	3.9	361

In accordance with the above result, it is apparent that the smaller the existing fraction of the rhombohedral structure is, the more will the lithium intercalation-deintercalation capacity be increased. In particular, [the] 5 existing fraction equal to or less than 10 % is desirable.

#### Embodiment 5

The present embodiment uses a cylindrical lithium secondary battery. A fundamental structure of the secondary 10 battery is shown in FIG. 8. In FIG. 8, the member [assigned with <sup>an</sup> ~~reference~~ <sup>identified by</sup>] 50 is a positive electrode. Similarly, a negative electrode 51, a separator 52, a positive electrode tab 53, a negative electrode tab 54, a positive electrode lid 55, a battery vessel 56, and a gasket 57 are shown.

15 The lithium secondary battery shown in FIG. 8 was prepared by the following steps. Mixed positive electrode agents slurry was prepared by mixing 88 % by weight in total solid of LiCoO<sub>2</sub> as an active material for the positive electrode, 7 % by weight of acetylene black as a conductive 20 agent, 5 % by weight of polyvinylidene fluoride (PVDF) as a binder, and N-methyl-2-pyrolidone.

Similarly, mixed negative electrode agents slurry was prepared by mixing 90 % by weight in total solid of the graphite powder of the present invention as an active 25 material for the negative electrode, 10 % by weight of polyvinylidene fluoride (PVDF) as a binder, and N-methyl-2-pyrolidone.

The mixed positive electrode agents slurry was applied onto both planes of a sheet of aluminum foil of 25  $\mu\text{m}$  [thick], and dried in<sup>1</sup> vacuum at 120 °C for one hour. After the vacuum drying, an electrode of 195  $\mu\text{m}$  [thick] was fabricated by roller 5 pressing. The average amount of the applied mixed agents per unit area was 55 mg/cm<sup>2</sup>. The positive electrode was prepared by cutting the aluminum foil [applied] with the <sup>applied</sup> mixed agents into a sheet [of] 40 mm in width and 285 mm in length. However, portions of 10 mm in length from both ends of the 10 positive electrode were not applied with the mixed agents for the positive electrode, the aluminum foil was bared, and one of the bared [portion] was welded to the positive electrode tab by ultrasonic bonding.

The mixed negative electrode agents slurry was applied onto both planes of a sheet of copper foil of 10  $\mu\text{m}$  thick, and dried in<sup>1</sup> vacuum at 120 °C for one hour. After the vacuum drying, an electrode of 175  $\mu\text{m}$  thick was fabricated by roller pressing. The average amount of the applied mixed agents per unit area was 25 mg/cm<sup>2</sup>. The negative electrode was prepared by cutting the copper foil [applied] with the <sup>applied</sup> mixed agents into a sheet [of] 40 mm in width and 290 mm in length. However, as [same as] the positive electrode, portions [of] 10 mm in length from both ends of the negative electrode were not applied with the mixed agents for the negative electrode, the copper foil was bared, and one of the bared portion was welded to the negative electrode tab by ultrasonic bonding.

A fine pored film made of polypropylene of 25  $\mu\text{m}$  thickness and 44 mm in width was used as a separator. The positive electrode, the separator, the negative<sup>electrode</sup>, and the separator were piled in the order described above, and the pile was 5 rolled to form a bundle of [the] electrodes. The bundle was contained in a battery vessel, the negative electrode tab was welded to the bottom of the battery vessel, and a drawn portion for caulking the positive electrode lid was fabricated. An electrolytic solution prepared by adding 10 lithium hexafluorophosphate by 1 mol/l into a mixed solvent containing ethylene carbonate and diethylcarbonate by 1:1 in volume was filled in the battery vessel, the positive electrode tab was welded to the positive electrode lid, and the positive electrode lid was caulked to the battery vessel to form the 15 battery.

Using the battery which had been prepared by the above steps, [the charge and discharge] were repeated under a condition [that] the charging and discharging current was 300 mA, and respective<sup>ones</sup> of the terminated potentials of the 20 charge and the [discharge was] 4.2 V and 2.8 V. Furthermore, the charging and the discharging [current was] varied in a range from 300 mA to 900 mA, and [the] rapid [charge] and rapid discharge<sup>ing</sup> were performed.

25 Comparative example 3  
provide comparison

In order to [compare] with the present invention, a lithium secondary battery was manufactured by the <sup>same</sup> method as

[same as the] embodiment 5 using the conventional graphite powder (the raw powder for the graphite powder of the present invention), and the battery characteristics [was] determined [as] same as [the] embodiment 5.

5 The result of comparison [on] the characteristics of the lithium secondary battery of the embodiment 5 (the present invention) and the comparative example 3 (prior art) [is] explained hereinafter.

FIG. 9 indicates variation in discharge capacity of the lithium secondary battery when the charge and discharge of the battery were repeated. The curve 60 indicates the discharge capacity of the embodiment 5. The curve 61 indicates the discharge capacity of the comparative example 3. In the embodiment 5, the maximum discharge capacity was 683 mAh, and [a] ratio in the discharge capacity after 200 cycles to the maximum capacity was 86 %. While, in the comparative example 3, the maximum discharge capacity was 492 mAh, and [a] ratio in the discharge capacity after 200 cycles to the maximum capacity was 63 %.

20 FIG. 10 indicates a relationship between the charging current and discharging current and the discharge capacity when [the] rapid charge and rapid discharge were performed. The curve 70 indicates the discharge capacity of the embodiment 5. The curve 71 indicates the discharge capacity of the comparative example 3. With [the] charging and discharging current of 900 mA, the discharge capacity of the embodiment 5 was 573 mAh, while the discharge capacity of the comparative example 3

was 256 mAh. The ratio of [decreasing] the discharge capacity in the respective <sup>ones</sup> of the present cases to the discharge capacity in the case of <sup>the</sup> charging and discharging current of 300 mAh/g were 16 % and 48 %, respectively. Therefore, [in] 5 [accordance with] using the graphite powder of the present invention as the active material for the negative electrode, the [decreasing] ratio of <sup>the</sup> capacity was improved by at least 30 %, and it became apparent that the lithium secondary battery relating to the present invention had an 10 excellent characteristics [in] rapid charge <sup>for</sup> and discharge <sup>ing</sup>.

#### Embodiment 6

Mixed positive electrode agents slurry was prepared using LiMn<sub>2</sub>O<sub>4</sub> as a positive electrode active material, and 15 the positive electrode was prepared by applying the mixed positive electrode agents slurry onto both planes of a sheet of aluminum foil [in the] <sup>the manner</sup> same as [the] embodiment 5. The average amount of the applied mixed agents per unit area was 65 mg/cm<sup>2</sup>, and the electrode thickness after fabrication by 20 roller pressing was 230 µm. The positive electrode was prepared by cutting the aluminum foil [applied] with the <sup>the</sup> mixed agents into a sheet [of] 40 mm in width and 240 mm in length. However, portions [of] 10 mm in length from both ends of the 25 positive electrode were not applied with the mixed agents for the positive electrode. The negative electrode was [as] same as the negative electrode prepared in the embodiment 5. Then, the lithium secondary battery of the present embodiment

was prepared by the same method as the embodiment 5, such as forming an electrodes bundle, inserting the electrodes bundle into a vessel, welding bottom of the vessel, adding an electrolytic solution, caulking a positive electrode lid, 5 and others.

Using the battery, charge and discharge were repeated under a condition of charging and discharging current of 300 mA, and the terminated potential of the charge and discharge of 4.2 V and 2.8 V, respectively. As [the] result, the maximum 10 discharge capacity was 581 mAh, and [a] ratio [in] the discharge capacity after repeating the charging and discharging reactions 200 cycles to the maximum discharge capacity was 84 %. The above result indicates that the charging and discharging characteristics of the present embodiment [is] 15 superior to the comparative example 3.

A lithium secondary battery which has a high energy density and [an] excellent charging and discharging characteristics can be obtained by using the graphite powder, which is superior in reversibility of the 20 intercalation-deintercalation reaction of lithium, of which the maximum particle size is less than 100  $\mu\text{m}$ , wherein the existing fraction of the rhombohedral structure in the crystalline structure is less than 20 %, as the active material for the negative electrode of the battery.